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THE ALUMINUM REDUCTION METHOD AS  
APPLIED TO THE DETERMINATION OF  
NITRATES IN "ALKALI" SOILS

BY  
PAUL S. BURGESS

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While the phenoldisulphonic acid method for determining nitrates in soils at present offers the most speedy and satisfactory means of ascertaining the nitrate content of soils free from "alkali," it has been shown<sup>1</sup> to be of questionable value when employed with soils containing even small amounts of soluble salts, and especially in the presence of the chlorides and sulfates of the alkalies. Since this is true, and further since the number of nitrate determinations on soils containing "alkali" is constantly increasing, due to the great increase in our research work on "alkali" problems, both chemical and bacteriological, it was deemed by the writer to be a matter of importance to establish a method for the determination of nitrates which was not affected by the presence of soluble salts.

The possible methods considered were Busch's "nitron" process, the methods depending upon the liberation and subsequent measuring of nitric oxide, and the reduction methods in which the nitrate nitrogen is reduced to ammonia and either titrated against a standard acid solution or Nesslerized.

Busch's "nitron" process<sup>2</sup> was rejected for the following reasons. A number of the acids (both organic and inorganic),

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<sup>1</sup> Univ. of Calif. Publ. Agr. Sci., vol. 1, no. 2, pp. 21-37. Utah Agr. Exp. Sta. Bull., 106.

<sup>2</sup> Ber. Deut. Chem. Gsell. 38 (1905), 3, pp. 861-866

and salts found in soils, form insoluble compounds with the "nitron" (1,4-diphenyl-3,5 endanilodihydrotryazol) as well as does the nitrate radicle. The sterilization of soils also appears to liberate substances which interfere with the crystallization of the "nitron" nitrate.<sup>3</sup> The occurrence of soluble organic matter invariably present in the soil solutions tends, in many cases, to vitiate completely the results.<sup>4</sup> The calcium oxid, which we use to coagulate the clay before filtration, comes down as the carbonate in the filtrate, thus making a gravimetric determination impracticable. (Lime has been shown to effect the *least* loss of nitrates of any of the common coagulants.) The trouble and cost of procuring the reagent also militated against the use of this method. The Schulze-Tiemann,<sup>5</sup> Schlösing-Wagner,<sup>6</sup> and similar methods which depend upon the liberation and subsequent measurement of the nitric oxide from the nitrates did not appear feasible because of the errors introduced through atmospheric conditions, the expense of apparatus for a large number of determinations, and the length of time necessary for the operations involved.

Thus all but the reduction methods were eliminated. In 1890 the Agricultural Experiment Station<sup>7</sup> at Halle, Germany, perfected a reduction method for the determination of nitrogen in nitrates. They used zinc dust, iron filings, and a solution (sp. gr. 1.3) of sodium hydrate. The presence of chlorides and sulfates did not impair the accuracy of the determination. Several modifications of this reduction process are now used. In the modified Ulsch<sup>8</sup> method sulfuric acid and reduced iron are employed to liberate the nascent hydrogen, an excess of magnesium oxid being added just before distillation. In the Devarda<sup>9</sup> method an alkali, an alloy of aluminum, copper and zinc, and ethyl alcohol are all used to effect the reduction. M. E. Pozzi-

<sup>3</sup> J. Litzendorff, *Ztschr. Angew. Chem.* 20 (1907), 51, pp. 2209-13.

<sup>4</sup> Mich. Exp. Sta. Rep. for 1911, pp. 178-181.

<sup>5</sup> Bohm, *Ztschr. Zuckerind.* 25 (1900), p. 356, abs. in *Chem. Centrbl.* (1901), I, 22, p. 1216.

<sup>6</sup> König's *Untersuch. Landw. Stoffe*, p. 151.

<sup>7</sup> Experiment Station Record, vol. V, pp. 464-465.

<sup>8</sup> New Jersey Exp. Sta. Rep. for 1892, pp. 188-193.

<sup>9</sup> *Analyst*, 35 (1910), 412, p. 307.

Escot<sup>10</sup> utilizes aluminum filings, mercuric chloride and a solution of potassium hydrate. J. T. Bornwater<sup>11</sup> uses aluminum filings and a solution of potassium hydrate.

Still further elimination was thus necessary among the reduction methods. The modified Ulsch method presented certain difficulties of technique which, in the case of numerous determinations, would render the method impracticable. The aluminum reduction method has been heretofore used successfully in water analysis,<sup>12</sup> and it appeared advisable to make a study of it as applied to determinations of large amounts of nitrates as met with in soil work; it further seemed important to determine the feasibility of its use for a large number of determinations made simultaneously. Such other factors also as the amounts of aluminum and of alkali to employ, the length of time, and the temperature for reduction, demanded a careful test.

#### DESCRIPTION OF THE METHOD

One hundred grams of the soil in which the nitrates are to be determined are placed in round-bottomed, enameled cereal dishes which have a capacity of about 800 c.c. Mortars were used at first, but the cereal dishes were found to be much lighter, easier to manipulate, and less expensive. Two grams of powdered CaO and exactly 200 c.c. of distilled water are added to each dish. The contents of each dish are now thoroughly ground and mixed with a pestle for from 3 to 5 minutes, after which the soil and clay are allowed to settle for 15 or 20 minutes, and are then filtered through paper. It may be said here that the solutions should never be allowed to stand over 2 to 3 hours, as there occurs a noticeable loss of nitrates, possibly due to dentrification. In case it is impossible to proceed at once with the determination a few drops of chloroform<sup>13</sup> may be added. One hundred c.c. portions of the filtrates, obtained as above described, are placed in 400 c.c. casseroles and 2 c.c. of a 50 per cent NaOH solution, free from nitrates, added to each. These are then boiled

<sup>10</sup> Ann. Chim. Analyt. 14 (1909), 12, pp. 445-446.

<sup>11</sup> Chem. Centbl. (1906), I, 8, p. 703.

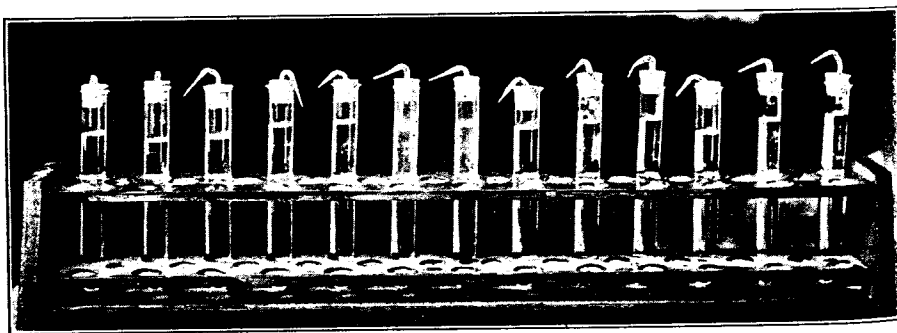
<sup>12</sup> Amer. Jour. Pub. Hyg., vol. XIX, 3, p. 1.

<sup>13</sup> V. I. Sazanov, Abs. in Centbl. Zuckerindus. 15 (1907), 34, p. 923.

down to about half their original volume to drive off ammonia, the residues washed into 125 c.c. Jena test tubes, diluted to 100 c.c., and a strip of aluminum (about  $150 \times 6 \times .4$  mm., weighing approximately one gram) added to each. The tubes are then stoppered with one-hole rubber stoppers carrying bent glass tubes, each of which has been drawn out to a fine capillary tip. The solutions are allowed to remain in the tubes from 11 to 14 hours at a constant temperature of from  $20^{\circ}$  to  $22^{\circ}$  C. (about our laboratory temperature). In case of large amounts of nitrogen the temperature is of prime importance, a lower temperature giving incomplete reduction in the above mentioned time, while a higher temperature may induce a considerable loss of ammonia. After reduction the contents of the test tubes are washed into distilling flasks, about 300 c.c. of distilled, ammonia-free water is added, and the ammonia distilled off and caught in N/10 HCl, the excess of acid being titrated against N/10  $\text{NH}_4\text{OH}$ .

We run 24 or 36 determinations simultaneously, avoiding a loss of time by allowing the reduction to take place over night, either in an incubator kept at  $20^{\circ}$ - $22^{\circ}$  C., or when temperature conditions are right, in the laboratory.

The ~~out~~ below shown is a photograph of a rack which the writer had made for the purpose of holding 36 of the large test tubes while reduction was taking place. The holes are all numbered, thus doing away with the necessity of marking the glass tubes, the determinations being run in rotation.



# TEST OF THE REDUCTION METHOD WITH LARGE QUANTITIES OF NITRATE

In soil work considerable amounts of nitrates are often encountered. The first series of experiments were thus made to determine whether or not the reduction method would prove accurate in the presence of from 30 to 60 mgs. of nitrate nitrogen.

The results set forth in the following table are averages of several analyses made at the same time and under similar conditions. A comparison is also made here of the reduction method with the phenoldisulphonic acid method.

TABLE I

A COMPARISON OF THE REDUCTION METHOD AND THE PHENOLDISULPHONIC  
ACID METHOD WITH LARGE AMOUNTS OF NITRATE NITROGEN

No.	Nitrate N added Mgs.	Reduction Method Nitrate N recovered Mgs.	Phenoldisulphonic Acid Method Nitrate N recovered Mgs.
1	100	97.86	97.00
2	50	49.00	48.25
3	25	24.22	25.40

We thus see that the reduction method, even where *no* salts are present, but where large amounts of nitrates are found, is slightly more accurate than the phenoldisulphonic acid method.

## THE EFFECT OF "ALKALI" SALTS ON THE REDUCTION METHOD METHOD

As stated above, in our research work on different "alkali" problems in soils, more especially in soil bacteriology, and plant physiology, considerable amounts of salts are often used in soils in which later the nitrate content must be ascertained. Besides it is frequently necessary to determine nitrates in soils of the arid regions which contain considerable quantities of "alkali." It is important therefore to ascertain if the method herein proposed is in any wise affected by salts. Therefore the following tests were carried out. The salts employed were "Baker's An-

alyzed Chemicals." All the reagents upon analysis were found to be free from nitrogen. The salts were added in solution from accurately graduated pipettes and burettes. The reduction period for all the samples was 11 hours at a temperature of 20°-22° C.

The following table shows the results obtained in a series of nitrate determinations made by the reduction method in the presence of "alkali." The details with reference to these determinations are also given in the table, and the figures are averages of closely agreeing duplicate or triplicate analyses. This statement applies also to the following tables.

TABLE II

## EFFECTS OF NaCl

NaCl added Grams	Nitrate N added Mgs.	Aluminum Reduction Method Nitrate N recovered Mgs.	Phenoldisulphonic Acid Method Nitrate N recovered Mgs.
0.2	100	97.90	79.50
0.2	50	49.10	43.00
0.2	25	24.50	20.75

EFFECTS OF Na<sub>2</sub>SO<sub>4</sub>

Na <sub>2</sub> SO <sub>4</sub> added Grams	Nitrate N added Mgs.	Aluminum Reduction Method Nitrate N recovered Mgs.	Phenoldisulphonic Acid Method Nitrate N recovered Mgs.
0.35	100	98.42	72.75
0.35	50	49.42	38.20
0.35	25	24.36	19.75

EFFECTS OF Na<sub>2</sub>CO<sub>3</sub>

Na <sub>2</sub> CO <sub>3</sub> added Grams	Nitrate N added Mgs.	Aluminum Reduction Method Nitrate N recovered Mgs.	Phenoldisulphonic Acid Method Nitrate N recovered Mgs.
0.1	100	98.14	86.25
0.1	50	49.42	42.50
0.1	25	24.50	25.20

TABLE II—(Continued)

## EFFECTS OF "MIXED ALKALI" SALTS

Salts added Grams	Nitrate N added Mgs.	Reduction	Acid Method
		Method Nitrate N recovered Mgs.	Nitrate N recovered Mgs. Phenoldisulphonic
0.2 NaCl	100	99.54	65.00
0.35 Na <sub>2</sub> SO <sub>4</sub>			
0.1 Na <sub>2</sub> CO <sub>3</sub>			
0.2 NaCl	50	50.05	33.00
0.35 Na <sub>2</sub> SO <sub>4</sub>			
0.1 Na <sub>2</sub> CO <sub>3</sub>			
0.2 NaCl	25	24.57	12.00
0.35 Na <sub>2</sub> SO <sub>4</sub>			
0.1 Na <sub>2</sub> CO <sub>3</sub>			

That the salts present have little effect on the accuracy of the determination by the reduction method, and the superiority of the latter over the phenoldisulphonic acid method, is clearly shown by a comparison of the last two columns in the foregoing table. Where large losses of nitrates are induced by the presence of NaCl and Na<sub>2</sub>SO<sub>4</sub> with the second named method, there are only slight losses when the reduction method is employed, and these are found by a comparison with Table I to be apparently due to other causes.

In most cases where the reduction method is used there are slight losses of ammonia, although in a few individual analyses all of the nitrogen was recovered. It may be stated here that several analyses were run on solutions containing 100 mgs. of nitrate nitrogen, placing rubber stoppers in the large reducing test tubes, carrying bent glass tubes as traps and connecting with test tubes containing 10 c.c. of N/10 HCl each. These were later titrated against N/10 NH<sub>4</sub>OH and the results added to the figures found by distillation. By using this extra process we were able to recover all the N as NH<sub>3</sub>, but it was not found to be necessary where the smaller amounts of nitrate were present. It should be remembered that in soil work over 30 mgs. of nitrate nitrogen per 100 grams of soil are infrequently found, and of this amount only an aliquot (one-half) is taken for the actual analysis. In nitrification work also, especially where the production of nitrates is intense, the difference between parallels is



often from one to one and one-half milligrams of nitrogen, or about the amounts which appear to be lost where large quantities of nitrates are determined by this method.

As a means of comparison, the same amounts of "alkali" salts and nitrate were added and the entire series analyzed by the phenoldisulphonic acid method. The results of this work are shown in the last column of Table II. The standard method here calls for the use of 2 c.c. of the phenoldisulphonic acid, but we found that even where *no* foreign salts were present, if the amount of nitrate nitrogen exceeded about 10 mgs. 4 c.c. were necessary to complete the reaction.

The results of tests of the colorimetric method where large amounts of nitrates were present, using respectively 2 and 4 c.c. of the phenoldisulphonic acid, follow:

TABLE III

No.	"Alkali" salts present	Nitrate N added Mgs.	Nitrate N recovered using 2 c.c. phenoldisul- phonic acid Mgs.	Nitrate N recovered using 4 c.c. phenoldisul- phonic acid Mgs.
1	0	100	58.00	97.00
2	0	50	35.00	48.25
3	0	25	23.60	25.40

To ascertain whether or not 4 c.c. portions of the acid were sufficient, 6 c.c. quantities were tried. No gains in the amount of nitrate nitrogen recovered here resulted. Four c.c. portions were employed in the experiments reported in Table II.

It is interesting to note that while my results confirm the work of Lipman and Sharp on the effects of NaCl and Na<sub>2</sub>SO<sub>4</sub> on the phenoldisulphonic acid method, they are partly at variance with them on the effects of Na<sub>2</sub>CO<sub>3</sub>. The investigators named found that the nitrate determination by the method mentioned was in no wise affected by Na<sub>2</sub>CO<sub>3</sub>, but it should be recalled that they employed comparatively small quantities of nitrates and carbonates and that in the presence of larger quantities the chances of error are magnified.

# THE EFFECT OF SOLUBLE ORGANIC MATERIALS ON THE REDUCTION METHOD

After having found that the soluble mineral salts had no effect on the accuracy of the reduction method, it was deemed advisable to ascertain whether or not the organic matter, which is always present in the soils to a greater or less extent, interferes with it. Such organic materials may be roughly divided into two great classes: the humates, or the salts of humic acid with the alkalies of the soil, and the soluble carbohydrate material. By simply tritulating the soil sample with pure water but a very small percentage of the former class of compounds is ever extracted, while soluble carbohydrates are present in soils only in exceedingly small quantities, except in rare cases. In these tests dried, water soluble humus and dextrose were used and two sets of experiments were run, in one of which the solution to be reduced contained .2 per cent of dried humus and the other of which contained 1 per cent of dextrose. The addition of humus produced a very dark brown solution, much darker in fact than any solution that can be obtained by tritulating, even soil high in humus, with water. The analytical procedure was the same as that above given and the results are expressed in Table IV, and represent averages of closely agreeing duplicates.

TABLE IV

## EFFECT OF SOLUBLE HUMUS

No.	Soluble humus added Grs.	Nitrate N added Mgs.	Nitrate N recovered Mgs.
1	0.2	100	95.62
2	0.2	50	48.86
3	0.2	25	24.36

## EFFECT OF DEXTROSE

No.	Dextrose added Grs.	Nitrate N added Mgs.	Nitrate N recovered Mgs.
1	1.0	100	96.60
2	1.0	50	48.44
3	1.0	25	24.50

These results show a slight loss where large amounts of nitrate were present, but the same also holds true above, as an examination of the foregoing tables will indicate. Therefore the losses, which are also in part explained above, are not to be attributed to the presence of excessive amounts of soluble organic materials. Besides, the losses brought about for the reasons indicated are of no serious practical import, since most soils seldom contain more than from 15 to 20 milligrams of nitrogen per 100 grams of soil.

#### THE TIME REQUIRED FOR COMPLETE REDUCTION AT A TEMPERATURE OF 20°-22° C.

That the time required for complete reduction should be accurately ascertained at a given temperature is obvious. The results given below are averages of analyses carried on simultaneously.

TABLE V  
THE EFFECT OF TIME ON THE PROCESS OF REDUCTION AT CONSTANT  
TEMPERATURE (20°-22° C.)

Hours Nitrate N added Mgs.	1	2½	4	6	8	9	10	11	12	15	24
	Nitrate N recovered Mgs.										
100	19.04	33.88	46.20	55.02	89.74	93.10	96.53	97.90	97.44	98.42	95.1
50	19.18	22.05	31.36	36.82	46.76	47.18*	49.14	49.10	48.86	49.42	49.1
25	14.35	17.71	.....	19.00	20.79	23.94	23.94	24.50	24.50	24.50	24.1

In all of these samples 0.2 per cent of NaCl was present. A study of this data shows 11 to 15 hours to be the optimum time limits for reduction at 20°-22° C. A longer time results in a slight loss of ammonia from the solutions containing the larger amounts of nitrogen, while less than 11 hours is too short to effect complete reduction.

#### THE EFFECT OF TEMPERATURE ON THE TIME NECESSARY FOR REDUCTION

Temperature is of vital importance, both in the accuracy of the determination and also on the time necessary for complete reaction. This is borne out by the following table.

TABLE VI

TIME OF REDUCTION 12 HOURS. TEMPERATURE CONSTANT AT 8° TO 10° C.

NaCl added Grams	Nitrate N added Mgs.	Nitrate N recovered Mgs.
.2	100	47.53
.2	50	28.42
.2	25	22.96

TIME OF REDUCTION 6 HOURS. TEMPERATURE CONSTANT AT 45° C.

NaCl added Grams	Nitrate N added Mgs.	Nitrate N recovered Mgs.
.2	100	80.93
.2	50	43.26
.2	25	22.12

We thus see that at a temperature of 45° C. the reduction was more nearly complete in 6 hours than it was at the end of 12 hours where the temperature was maintained at 10° C. By means of a series of experiments similar to those shown in Table IV it is readily possible to find the optimum length of time for complete reaction at any given temperature.

#### AMOUNT NaOH SOLUTION REQUIRED

By another series of experiments, in which the traps above mentioned were used and different amounts (varying from 1 to 5 c.c.) of the 50 per cent NaOH solution added, we found that 2 c.c. of the latter gave the best results. One c.c. evidently did not generate hydrogen in sufficient quantities for complete reduction (especially in the presence of the larger amounts of nitrate), while the 4 and 5 c.c. portions made the solutions so alkaline as to effect the escape of considerable amounts of ammonia.

#### GENERAL REMARKS

The results obtained in the experiments described above are considered a valuable contribution to our methods of chemical and biochemical soil analysis, because they establish, on a practical basis, a method for the determination of nitrates in soils which yields accurate results, regardless of the condition of the soil which is examined. While for rapid determinations the reduction method is not found as serviceable as the phenoldisulphonic acid method, it replaces the latter for work on "alkali" bearing soils where it alone can be safely employed.

Moreover, the writer's results are also proof of the fact, as the data in Table I indicate, that even in the *absence* of salts the reduction method is superior to the colorimetric method where large quantities of nitrates are concerned.

In the case of soils containing large amounts of organic matter the reduction method is again found superior, since it is frequently found impossible to remove the color of a soil extract from such soils without a loss of nitrates.

So far as my investigations have gone on the subject, and I have tried to take into consideration the several factors involved, no uncontrollable factor has been found to militate against the successful use of the aluminum reduction method. Great accuracy can be obtained by taking the precautions above described, and reasonable accuracy may be assured in ordinary work without the use of such extraordinary measures. The method is strongly commended to the attention of soil investigators in all phases of the work and it is to be hoped that it may serve to render simple and free from annoyance the determination of nitrates in soils under circumstances which until now have presented many difficulties.

### CONCLUSIONS

1. The aluminum reduction method for the determination of nitrates in soils yields the most accurate results of all methods now commonly in vogue.

2. "Alkali" salts do not in any way interfere with the successful operation of the method.

3. The presence of extraordinarily large amounts of soluble organic materials (soluble humus and dextrose) have little effect on the method.

4. A temperature of 20° C. for from 11 to 15 hours has been found the optimum for the reduction of large quantities of nitrates.

5. The proper amount of NaOH to be employed in the reduction was found to be 2 c.c. of a 50 per cent solution, with an aluminum strip weighing approximately one gram.

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